Mater. Res. Soc. Symp. Proc. Vol. 864 © 2005 Materials Research Society

A pulsed EDMR study of charge trapping at P_b centers

Christoph Boehme, Felice Friedrich and Klaus Lips
Hahn-Meitner-Institut Berlin, Abteilung Siliziumphotovoltaik, Kekuléstr. 5,
12489 Berlin, Germany

ABSTRACT

Low temperature pulsed electrically detected magnetic resonance (pEDMR) measurements of charge trapping and recombination transitions involving P_b centers at the c-Si (111) /SiO_2 interface are presented. The results of these experiments show that when a conduction electron is trapped, it forms a strongly coupled spin pair with the defect electron prior to its readjustment into the charged P_b^- ground state. The data reveals that the Landé factors of the two electrons within these pairs are almost identical (difference < 0.002) and that they are, within the measurement accuracy, identical to the Landé factor of the uncharged, singly occupied P_b center. From this, it is concluded that trapping and recombination at P_b defects is dominated by direct charge capture and not by tunneling or hopping transitions from other localized states. Different cross sections attributed in previous studies to different interface defects at the c-Si/SiO_2 interface can be explained by readjustment out of different spin configurations of the charged P_b^{-*} defect.

INTRODUCTION

Recombination in the Shockley-Read-Hall (SRH) model consists of subsequent trapping of either a conduction electron into an unoccupied defect state followed by hole trapping into an occupied defect or vice versa. The trapping rate coefficients (= the capture probabilities per defect) in the SRH model are quantified by the incoming charge carrier flux times the capture cross section σ which can be defined as the geometrical cross section A of a defect times the probability p that a charge carrier which passes the defect is captured. When Shockley and Read [1] discussed the applicability of their recombination model first, they pointed out, that a direct capture of charge carriers into defects can only be justified if the charge carrier that encounters a defect and that may or may not become trapped, undergoes a certain readjustment time during which the system decides whether trapping occurs or not. For the application of the SRH model, the readjustment process is usually not important since it oftentimes takes place on negligible time scales which is why many (in fact most) of those studies which have taken advantage of the SRH model do not even mention their existence. In contrast to this, the understanding of a readjustment mechanism can explain the qualitative and quantitative nature of a given trapping process.

For the study presented here, the nature of conduction electron trapping and thus, also the nature of conduction electron readjustment at P_b centers are investigated. P_b centers are highly localized unsaturated silicon bonds at the technologically important crystalline silicon (c-Si) to silicon dioxide (SiO_2) interface. They are singly occupied and therefore paramagnetic states with strong anisotropy (almost pure p-states, [2,3]) and energy levels close to the middle of the silicon band gap which is why they are recombination centers. Many studies have been conducted on the properties of P_b centers in the past. In spite of this, there are still remaining questions about the mechanisms of charge carrier capture, readjustment and trapping. The study presented here is

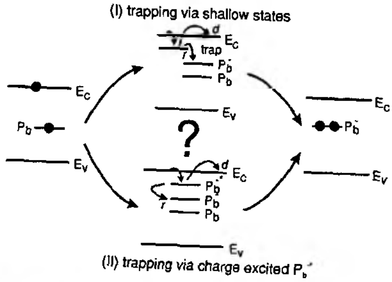

Figure 1: The Si band gap before (left) and after (right) a conduction electron has been trapped at a P_b center of the c-Si/SiO_2 interface. For the trapping process, two mechanisms are conceivable: (I) localization at a shallow trap state induced by another structural defect and subsequent readjustment; (II) localization in a charged excited P_b state (P_b^{-*}) and subsequent readjustment.

dedicated to the question of how conduction electrons at the c-Si/SiO_2 interface are captured into the P_b center. As sketched in fig. 1, before being captured, a conduction electron is in a delocalized conduction band state, while a strongly localized electron occupies the uncharged P_b center. After being captured, the conduction electron has become strongly localized as well and it shares a common charged P_b^- ground state with the second electron. It is known that the correlation energy between the two electrons in a charged P_b center is positive and hence, the P_b^- ground state has a slightly higher energy but can still be considered a deep state within the Si band gap [4]. The question to be answered is what happens with the conduction electron when trapping takes place? Given the success of the SRH model for the description of electron trapping at P_b centers it is reasonable to assume that readjustment must take place. If readjustment is present, what is the intermediate state of the charge carrier and defect electron pair as long as it has not decided whether the charge carrier will pass or remain trapped? – The relevance of this question becomes obvious when the two conceivable possibilities sketched in fig. 1 are considered: Trapping of the conduction electron begins by localization at (I) a shallow defect in proximity of the P_b center or (II) a shallow charged excited state of the P_b center (a so called P_b^{-*}). Both possibilities are then followed either by dissociation of this electron pair when the charge carrier is not trapped and reemitted into the conduction band at probability d or when the electron is trapped by readjustment into the P_b^- ground state with probability r. Note that depending on which of the two possibilities dominate trapping at P_b centers, both trapping and recombination rates will have different dependencies on the P_b density: For process (I), trapping rates are always determined by both, the P_b density and the shallow state density which means that P_b capture cross sections $\sigma = Ar/(d+r)$ (as explained by Rong et al. [5]), are highly dependent on the microscopic environment – when process (II) dominates, trapping at P_b centers requires P_b centers only and thus, their capture cross section is an inherent value, independent of the local environment.

EXPERIMENTAL APPROACH

In order to answer the question for the dominant trapping mechanism, an experimental approach must be used that is able to distinguish trapping via different defect states from direct capture into charged excited states. Traditional density of state measurement techniques such as deep level transient spectroscopy, capacitance voltage (CV) or modulated CV cannot discriminate the two alternative scenarios since only energy levels but not additional microscopic properties of the associated electronic states can be resolved. Hence, a different experimental approach is taken here, which has successfully been applied before to the investigation of silicon dangling bond trapping and recombination in hydrogenated microcrystalline silicon [6]. It is based on the determination of the Landé (g) factors of the two spins within the electron pair. If both electrons exhibit the same g-factor, it is conceivable that there must be two electrons within the same state, if this g-factor resembles the values and anisotropy of the P_b center, it shows that both electrons are contained in a single P_b center. In contrast, if the two spins within a pair resemble (i) the g-factor and anisotropy of P_b centers and (ii) a different g-factor close to $g = 2$ or below, it can be concluded that the pair consists of different types of defects, the P_b center and a shallow defect on the other hand [7].

Traditionally, the measurement of g-factors is a subject of electron spin resonance (ESR) spectroscopy. Many ESR studies have been conducted on the c-Si/SiO_2 interface (summarized elsewhere [8]) including the discovery of the P_b center by Nishi in 1971 [9]. For the problem to be solved here, ESR is not the right method: While ESR may identify P_b centers, it is not able to discriminate between those centers that do and those that do not participate to trapping processes nor can it provide information about transition rates. In addition, while ESR in principle should by able to detect the trapping partners of P_b centers, one can not distinguish whether and how a detected ESR resonance interacts with a P_b center nor is it possible to conclude from a single ESR spectrum, whether the resonances contained therein are at the c-Si/SiO_2 interface at all or whether they may even belong to other parts of the sample (e.g. bulk, sample edges etc.).

The experimental way to identify the spin partners of P_b centers and their g-factors during charge carrier trapping is pulsed electrically detected magnetic resonance (pEDMR). PEDMR is the transient measurement of conductivity changes after spin-dependent transport or recombination rates have been changed due to a short, coherent (pulsed) electron spin resonant excitation. "Short" in this regard means shorter than the transition- and coherence times of the electrons that are to undergo transitions. By measurement of the sample current at an arbitrary time $t_{\mu s}$ after the pulse as a function of the excitation pulse length τ, the coherent spin motion of the magnetic resonance excited spins can be extracted. Note that PEDMR just like the conventional continuous wave (cw) EDMR, is extremely sensitive to those spin centers involved in transport or recombination transitions. To all other paramagnetic centers it is not sensitive. By excitation of the appropriate g-factor, defined transitions can be highlighted selectively. Moreover, in contrast to cw EDMR, the transient measurement of the exited transitions with pEDMR allows access to information about g-factor differences of the pair partners involved in a selected transition. More information about the potential and the experimental foundations of pEDMR are outlined elsewhere [10-12].

EXPERIMENTAL DETAILS

For the experiments, a native oxide layer between interdigited lateral contact grids was used. The sample substrate was a lightly n doped ([P] $\approx 4 \times 10^{13}$ cm^{-3}) Czochralski-Si wafer. For the preparation of the oxide, it was cleaned with a standard RCA procedure and then subjected for 1

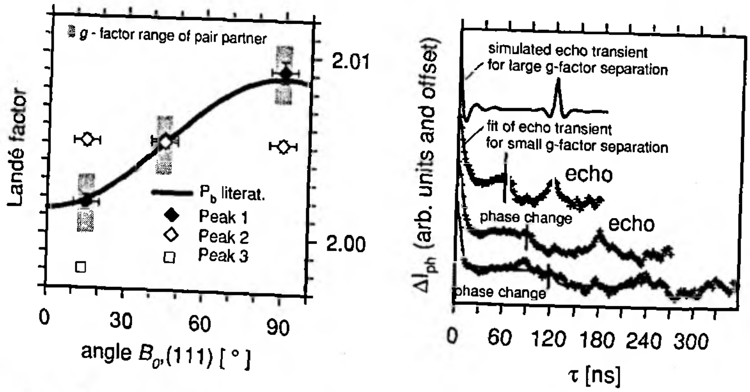

Figure 2: Left: g-factors of pEDMR resonances after a pulse with length $\tau = 64$ns and power $P = 24$W. The solid line represents the literature values [8] of the P_b center. Right: The PC after the pulse of $P = 64$W that was on resonance with peak 1 as a function of τ when sudden (ps scale) 180° phase changes are introduced after τ = 60ns, 90ns and 120ns. One can see an echo effect for 60ns and 90ns. For the 120ns plot, the echo is hardly visible due to incoherence. The three plots were fit (solid black lines) by theoretical transients for tightly coupled pairs of spins with similar g-factors ($\Delta g < B_1$) [10]. For a comparison, a simulation of an echo transient for $\Delta g > B_1$ is plotted which does not exhibit the second dephasing after the phase. Thus, an estimate of the g-factor range of the two pair partners associated with peak 1 was possible as indicated by the gray boxes on in the left plot ($\Delta g < B_1 < 0.002$).

min. to a 1% HF dip. Right after this treatment, a 300nm thick Al layer was deposited with electron beam evaporation which was then structured with standard photolithography into an interdigited contact system. After the contact preparation, the Si surface between the contacts was exposed for 24 hours to dry air at room temperature such that a thin native oxide layer could grow.

For the pEDMR experiments, a steady state photocurrent (PC) was induced by illumination with infrared and ultraviolet filtered white light of a halogen lamp and application of a constant voltage of $U = 4$V. The temperature was kept at $T = 15$K to reduce spin-lattice relaxation. The coherent microwave pulses for the magnetic resonant excitation were generated by an X-Band (9.7 GHz) Bruker E580 spectrometer. The PC transients were recorded for different magnetic fields B_0, different angles between the orientations of B_0 and the (111) orientation of the sample surface as well as different pulse lengths τ.

EXPERIMENTAL RESULTS

PEDMR spectra are the PC changes measured right after the coherent pulse (that means after the amplifier rise time is reached) as a function of the magnetic field B_0. The pEDMR spectra for the sample described above could be fit with three gaussian peaks (not shown here) whose dependence on the angle between the (111) direction and B_0 is displayed in fig. 2 (left). One can clearly see that one peak exhibits an anisotropy which compares to the P_b center literature values

[8]. Thus, by measuring with an excitation of $g \approx 2.009$ while B_0 is perpendicular to the (111) direction, one can selectively measure influences by P_b transitions only without any contributions of the isotropic resonance $g \approx 2.005$ and or the resonance at $g \approx 1.998$ whose influence on P_b transitions will be discussed below. From the PC response at $g \approx 2.009$, the dynamics of the P_b recombination on a ns time scale was extracted. This was done with a recombination echo experiment which is the detection of rephasing Rabi-oscillation by means of pulse length dependence measurements of the PC measured right after the pulse. The results of three of such recombination echo experiments are displayed in fig. 2 (right): The data essentially reflects the recombination rate through the P_b center during the pulse when sudden 180° phase changes are introduced at $\tau = \tau_{180} = 60$ns, 90ns and 120ns. Right after the pulse begins at $\tau = 0$, a strong decrease of the PC (increase of recombination) takes place. After about $\tau \approx 30$ns, the spin-Rabi oscillation responsible for this change has dephased and the PC remains constant. Then, after the phase jump, a second dephasing occurs, before a brief temporary rephasing (the recombination echo effect) becomes visible at $\tau = 2\tau_{180}$. Note that the echo is most pronounced for the experiment with $\tau_{180} = 60$ns and least for $\tau_{180} = 120$ns. The data was fit with theoretical recombination echo transients as predicted for strongly coupled spin pairs and a non-negligible coherence decay. The fit results are represented by the black line under the data crosses of fig. 2. They show a reasonable agreement with the experimental data and reveal for all three echo transients a decay factor of $r_3 = 1.6(2)\text{x}10^6\text{s}^{-1}$ which explains why the echo of the transient with $\tau_{180} = 120$ns is hardly visible. The variable r_3 was chosen in accordance with the nomenclature of Ref.[10] .

DISCUSSION AND CONCLUSIONS

PEDMR theory [10] predicts that the dephasing after the microwave phase change is only possible when the Larmor separation (= g-factor difference Δg in magnetic field units, $\Delta g/(\mu_B h\nu)$, $\nu \approx 9.7$ GHz is the microwave frequency) of the two spins in the electron pair is smaller than the applied B_1 field (= the magnetic field strength of the exciting microwave radiation). If $B_1 < \Delta g/(\mu_B h\nu)$, an echo transient without second dephasing can be expected. A simulation of such a transient is plotted in fig. 2 (right), it does not agree with the experimental data. In contrast, the fits results of the experimental data with an echo transient for which strong coupling (small Larmor separation) was assumed, shows excellent agreement. One can conclude that since $B_1 < 400\mu$T, the g-factor difference of the spin pair around $g = 2.009$ is $\Delta g < 0.002$ and, therefore, the other resonances found at $g \approx 2.005$ and $g \approx 1.998$ can not be due to weakly coupled pair partners of the P_b center. Note that the gray bars around the Peak 1 data in fig. 2 (left) indicate the g-factor range in which one would expect the g-factor of the pair partners. Except for a sample angle of 45° where the P_b resonance crosses $g = 2.005$, there is no agreement between any of the two other resonance and the gray ranges. We conclude from this that the two resonances at $g \approx 2.005$ and $g \approx 1.998$ are not involved in the trapping and recombination of the P_b center and theferefore, the conduction electrons localized at the P_b center must exhibit the P_b anisotropy known from ESR at singly occupied P_b states during the time span from the localization of the conduction electron to readjustment. Hence, both electrons localized at the P_b site before readjustment, exhibit the anisotropy of the P_b state, yet they are not in a P_b^- ground state. We conclude from this, that they exist in a charged exited P_b^{-*} state. With this interpretation, and the nomenclature of Ref. [10], one can attribute the time constant r_3 to the readjustment time of the P_b center.

Note that the spin-dependency of the P_b center readjustment implies that the measured coherence decay time is not the only readjustment time, but the fasted readjustment time, the readjustment out of P_b^{-*} in singlet states. Beside the singlet readjustment, there is also the much slower triplet readjustment which determines the decay of the pEDMR signal after the pulsed excitation. The triplet readjustment time which is discussed elsewhere [14] has a rate coefficient of $r_T = 1.9(1)\times10^3 s^{-1}$. For the capture cross section that was defined by SRH to be proportional to the readjustment rates (as explained above), this implies that a single P_b center may capture electrons at different capture cross sections that vary by more than two orders of magnitude. The value that applies when an electron is trapped depends on the mutual spin orientation of the defect and the conduction electron upon encounter. An effect that may be an explanation for two different capture cross sections at the c-Si/SiO_2 interface observed by Albohn et al. [4].

SUMMARY

It was shown that trapping of conduction electrons at P_b centers of the c-Si/SiO_2 interface is possible by direct capture through charged exited states. This shows that charge carrier trapping and recombination at P_b centers at the c-Si/SiO_2 interface is an inherent property of these defects and it does not require the presence of additional defects such as shallow traps. It has to be emphasized that the proof of direct capture recombination into a charged excited state at the P_b center is not proof that other capture mechanisms such as shallow trap assisted processes do not exist. They may exist and could be involved in the other observed resonances.

REFERENCES

1. W. Shockely, W. T. Read jr., *Phys. Rev.* 57 (5), 835 (1952).
2. K. L. Brower, *Appl. Phys. Lett.* 43, 1111 (1983).
3. M. Cook and C. T. White, *Phys. Rev. B* 38, 9674 (1988).
4. J. Albohn, W. Füssel, N. D. Sinh, K. Kliefoth, and W. Fuhs, J. Appl. Phys. 88, 842 (2000).
5. F. C. Rong, W. R. Buchwald, E. H. Poindexter, W. L. Warren, and D. J. Keeble, Solid State Electron. 34, 835 (1991).
6. C. Boehme and K. Lips, *Phys. Status Solidi* C 1, 1255 (2004).
7. J. M. Spaeth, H. Overhof, *Point Defects in Semiconductors and Insulators*, Springer Verlag Berlin (2003).
8. P. M. Lenahan and J. F. Conley, J. Vac. Sci. Technol. B 16, 2134 (1998).
9. Y. Nishi, Jpn. J. Appl. Phys. 10, 52 (1971).
10. C. Boehme and K. Lips, *Phys. Rev. B*, 68 (24), 245105 (2003).
11. C. Boehme and K. Lips, *Phys. Rev. Lett.*, 91 (24), 246603 (2003).
12. C. Boehme and K. Lips, *Appl. Phys. Lett.* 79, 4363 (2001).
13. C. Böhme, *The dynamics of spin-dependent charge carrier recombination*, Cuvillier Verlag, Göttingen (2003).
14. F. Friedrich, C. Boehme and K. Lips, J. Appl. Phys. 97, 056101 (2005).